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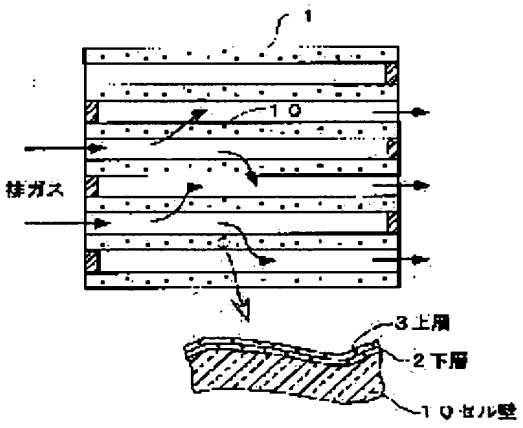
(71)Applicant : TOYOTA MOTOR CORP
(72)Inventor : OGURA YOSHITSUGU

(54) PARTICULATE FILTER

(57)Abstract:
PROBLEM TO BE SOLVED: To suppress the deterioration of combustion performance of a particulate caused by the decrease of a noble metal carrying amount, and also suppress the sulfur poison of an NOX occlusion material.
SOLUTION: A lower layer 2 which is formed by making an oxide carrier carry the NOX occlusion material and noble metal, and an upper layer 3 which is formed by making an oxide having an oxygen storing/discharging capacity carry the noble metal, are formed on a cell wall 10 comparting the cells from each other. By separating the upper layer having the function of burning the particulate and the lower layer having the function of controlling NOX emission, the sulfur poison is suppressed, the activity deterioration of noble metal caused by the occlusion material is also suppressed, and the combustion of the particulate is accelerated by including the oxide having the oxygen storing/discharging capacity.



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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] Nothing and these two or more cels are blockaded in the shape of a checker in respect of an end in abbreviation tubed with two or more cels prolonged in parallel mutually. This cel that is not blockaded in respect of the end is the particulate filter which is blockaded in respect of the other end and it comes to blockade in the shape of a checker also in respect of the other end, and to the cell wall which divides these cels It is NOx to oxide support. Particulate filter characterized by forming the lower layer which comes to support occlusion material and noble metals, the upper layer which came to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in this lower layer front face, and the catalyst bed which becomes more.
[Claim 2] the oxide which has said oxygen occlusion emission ability -- CeO2 and CeO2-ZrO2 multiple oxide and CeO2-ZrO2-aluminum 2O3 a multiple oxide -- and -- Particulate filter according to claim 1 which is chosen from Fe 2O3 and which is a kind at least.
[Claim 3] The amount of support of said noble metals is a particulate filter according to claim 1 with more upper one than a lower layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is arranged on the emission way of a diesel power plant etc., and relates to the particulate filter which has a catalyst function in detail about the particulate filter which carries out uptake of the particulate in exhaust gas.
[0002]
[Description of the Prior Art] In order to carry out uptake of the particulates, such as soot in exhaust gas, the diesel particulate filter (henceforth DPF) is arranged conventionally on the emission way of a diesel power plant. This DPF is formed in a honeycomb configuration from heat-resistant ceramics, such as cordierite, the cel which is not blockaded in respect of the end is blockaded in respect of the other end, and two or more cels (honeycomb path) are blockaded in the shape of a checker also in respect of the other end while being blockaded in the shape of a checker in respect of an end.
[0003] It flows into the outflow side edge side which passes the septum which constitutes a cel from this DPF since that cel is blockaded in respect of the outflow side edge and the exhaust gas which flowed into the inflow side edge side from the cel which carries out opening is difficult to come out from an outflow side edge side as it is, and adjoins out of the cel which is carrying out opening. Therefore, uptake of the particulate in exhaust gas is carried out on a septum or into a septum by the filtration at the time of passing a septum, and the exhaust gas which does not contain a particulate flows out of an outflow side edge side by it.
[0004] By the way, the particulate by which uptake was carried out on a septum or into the septum is deposited gradually, by this, blinding will arise to a septum and ventilation resistance will become large. Then, by heating periodically or passing hot exhaust gas, cleaning which burns the deposited particulate and recovers filtration is performed.
[0005] Then, giving an emission-gas-purification catalyst function to DPF is also performed by it not only burning a particulate, but supporting catalyst metals, such as platinum, to a septum, carrying out oxidative degradation of the hydrocarbon and carbon monoxide in exhaust gas, and understanding some nitrogen oxides a returned part by the catalysis. Thus, since a deposited particulate combustion temperature falls according to DPF which supported the catalyst metal, combustion removal of the particulate can be carried out at exhaust gas temperature, and DPF can be reproduced continuously.
[0006] For example, the continuation playback type DPF which supported alkaline earth metal and a platinum metal to the cell wall of DPF is proposed by JP,7-106290,B. Moreover, in JP,9-094434,A, it is NOx in the pore of a cell wall. According to [DPF which supported occlusion material is proposed and] this DPF, they are particulate continuation oxidation and NOx. It is indicated that it can purify.
[0007] However, exhaust gas temperature in the usual transit region from a diesel power plant In order to reproduce continuously 150 to 500 degree C, and the particulate deposited using DPF of the above-mentioned continuation playback type since it was low in exhaust gas, the high oxidation rate was needed in the low exhaust gas temperature field, and the amount of support of noble metals had to be made [many]. Therefore, a price becomes high and DPF of a continuation playback type serves as hindrance of the spread of them.
[0008] Moreover, noble metals and NOx At the continuation playback type DPF which supported both occlusion material, it is NOx at the time of use. There is fault that occlusion material moves and the activity of noble metals falls the front face of noble metals to a wrap sake. Furthermore, it is NOx. Occlusion material carries out occlusion also of the sulfur oxide in exhaust gas, serves as a sulfate, and is NOx. There was also a problem that occlusion ability disappeared. This phenomenon is called sulfur poisoning.

[0009]
[Problem(s) to be Solved by the Invention] This invention is NOx while being made in view of such a situation and controlling the fall of the particulate flammability ability accompanying reduction of the amount of support of noble metals. It aims at controlling sulfur poisoning of occlusion material.
[0010]
[Means for Solving the Problem] The description of the particulate filter of this invention which solves the above-mentioned technical problem Nothing and two or more cels are blockaded in the shape of a checker in respect of an end in abbreviation tubed with two or more cels prolonged in parallel mutually. The cel which is not blockaded in respect of the end is the particulate filter which is blockaded in respect of the other end and it comes to blockade in the shape of a checker also in respect of the other end, and to the cell wall which divides cels It is NOx to oxide support. It is in the lower layer which comes to support occlusion material and noble metals, the upper layer which came to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in it on the surface of the lower layer, and the catalyst bed which becomes more being formed.
[0011] the oxide which has oxygen occlusion emission ability -- CeO2 and CeO2-ZrO2 multiple oxide and CeO2-ZrO2-aluminum 2O3 a multiple oxide -- and -- The thing which is chosen from Fe 2O3 and which is a kind at least is desirable. Moreover, as for the amount of support of noble metals, it is desirable for there to be more upper one than a lower layer.
[0012]
[Embodiment of the Invention] It is NOx to oxide support in the cell wall which divides cels in the particulate filter of this invention. The lower layer which comes to support occlusion material and noble metals, the upper layer which came to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in it on the surface of the lower layer, and the catalyst bed which becomes more are formed. Therefore, NOx Since it is contained only in a lower layer and has not expressed on an emission way, occlusion material is NOx. The contact probability of occlusion material and a sulfur oxide is reduced, sulfur poisoning can be controlled, and it is NOx even with after [high] durability. Decontamination capacity is discovered.
[0013] Moreover, since noble metals are supported with the upper layer by the oxide which has oxygen occlusion emission ability, particulate combustion is promoted by the absorption/emission of oxygen. And in the upper layer, it is NOx. Since occlusion material is not contained, noble metals are NOx. Fault which is covered by occlusion material and deactivates is prevented, and the activity of noble metals is discovered by max. The amount of support of noble metals can be reduced by this, and suppose that it is cheap. And deposition can be followed, a particulate can be burned and a particulate filter can be reproduced continuously.
[0014] Conventional DPF formed from heat-resistant ingredients, such as cordierite and silicon carbide, can be used for the base of the particulate filter of this invention. What is necessary is just to design the magnitude, the number of cels, porosity, an average pole diameter, etc. according to the purpose.
[0015] The pore of an one to 100 micrometer aperture is formed innumerably, and while being able to pass a cell wall from the cel by the side of emission close to the cel by the side of emission appearance, and exhaust gas's being able to circulate and securing permeability because they are open for free passage, it has the structure where a particulate can be filtered at the cell wall which divides two or more cels. And the catalyst bed which becomes a cell wall from a lower layer and the upper layer is formed, and this catalyst bed is formed in the inner circumference front face of the above-mentioned pore, and the inner circumference front face of a cel.
[0016] A lower layer is NOx supported by oxide support and oxide support. It consists of occlusion material and noble metals. Two or more sorts of multiple oxides chosen from kinds, such as aluminum 2O3, and TiO2, ZrO2, SiO2, CeO2, two or more sorts, or these as oxide support can be used. Specific surface area was highly excellent in thermal stability especially. aluminum 2O3 is desirable. Moreover, if TiO2 etc. is used, since solid acid nature is strong and contiguity of a sulfur oxide will be controlled, it is NOx. Sulfur poisoning of occlusion material can be controlled further.
[0017] NOx supported by the lower layer As occlusion material, it can choose from rare earth metals, such as alkaline earth metal, such as alkali metal, such as K, Na, Li, and Cs, and Ba, calcium, Mg, Sr, and La, Pr, Nd, Sm, and can use. It is NOx especially. Alkali metal with high occlusion ability is used preferably. Moreover, it is desirable to be able to choose from Pt, Rh, Pd, Ir, Ru, Au, etc., to be able to use as noble metals, and to use Pt with oxidation activity high especially at least.
[0018] As for the lower layer amount of coats, it is desirable to consider as the range per [50-150g] 1l. of

filter base objects. It is NOx if there are few amounts of coats than this range. If occlusion material and the amounts of support of noble metals come to run short and it becomes thicker than this range, the path of the pore which exhaust gas passes will become small, and a pressure loss will increase.
[0019] Moreover, NOx in a lower layer The amount of support of occlusion material is good to consider as 0.01-0.5 mols per 1l. of filter base objects. NOx It is NOx if there are few amounts of support of occlusion material than this. If decontamination capacity runs short and it supports mostly from this, a wrap probability will become high about the noble metals supported by the lower layer, and the activity of noble metals will come to fall.
[0020] And the amount of support of the noble metals in a lower layer has 1 - 3% of the weight of the desirable range to a lower layer. It is NOx if there are few amounts of support of noble metals than this range. If decontamination capacity runs short and it supports mostly from this, the support consistency within a lower layer is too large, at the time of an elevated temperature, grain growth will come to arise in noble metals, and activity will fall.
[0021] The upper layer consists of an oxide which has oxygen occlusion emission ability, and noble metals supported by this oxide. although this oxide can be used if it has oxygen occlusion emission ability -- CeO2 and CeO2-ZrO2 multiple oxide and CeO2-ZrO2-aluminum 2O3 a multiple oxide -- and -- Especially the thing that is chosen from Fe 2O3 and that is a kind at least is desirable. It is because especially these oxides are excellent in oxygen occlusion emission ability and it excels also in endurance.
[0022] It is desirable to be able to choose from Pt, Rh, Pd, Ir, Ru, Au, etc., to be able to use as noble metals supported by the upper layer, and to use Pt with oxidation activity high especially at least.
[0023] As for the upper amount of coats, it is desirable to consider as the range of per [10-50g] 1l. of filter base objects. If there are few amounts of coats than this range, the amounts of support of noble metals come to run short, if it becomes thicker than this range, the path of the pore which exhaust gas passes will become small, and a pressure loss will increase. Moreover, since exhaust gas stops being able to reach a lower layer easily, it is NOx. Decontamination capacity will also fall.
[0024] In order to raise particulate oxidation activity, as for the amount of support of the noble metals in the upper layer, it is desirable to make [many] it, 1 - 10% of the weight of its range is desirable to the upper layer, and especially its 5 % of the weight or more is more desirable than a lower layer. If there are few amounts of support of noble metals than this range, particulate oxidation ability runs short of, if it supports mostly from this, the support consistency within the upper layer will be too large, and activity will fall with the grain growth at the time of an elevated temperature. The same noble metals as a lower layer may be supported, and different noble metals can also be supported.
[0025] After slushing the slurry of the above-mentioned oxide powder in a cel from an end side, making it adhere to a cell wall by drawing in from an other end side and calcinating it in order to form a lower layer or the upper layer for example, it is the noble metals or NOx of the specified quantity. What is necessary is just to support occlusion material. Moreover, it can also be made to adhere to a cell wall similarly using the slurry formed from the oxide powder which supported noble metals beforehand.
[0026]
[Example] Hereafter, an example and the example of a comparison explain this invention concretely.
[0027] (Example 1) The outline configuration of the particulate filter of this example is shown in drawing 1 . This particulate filter consists of a base 1 which consists of cordierite, a lower layer 2 formed in the cell wall 10 of a base 1, and the upper layer 3 formed in the front face of a lower layer 2. The base 1 is making the honeycomb configuration in which the cel with which opening was carried out to the inflow side edge side, and the outflow side edge side was taken up in checkers, and the cel which an inflow side edge side is taken up in checkers, and carries out opening in respect of an outflow side edge were formed by turns. In addition, the important section enlarged drawing of the cell wall 10 in drawing 1 shows the interior of the pore which can pass exhaust gas. Hereafter, the manufacture approach of this particulate filter is explained and it replaces with detailed explanation of a configuration.
[0028] As a base 1, it is a diameter. 100mm, die length 150mm DPF made from cordierite was prepared. The average pole diameter of this DPF is 30 micrometers, and porosity is 60%.
[0029] To a degree 2Oaluminum3 powder The 100 weight sections and TiO2 powder After mixing the 100 weight sections, the ZrO2 powder 20 weight section, the alumina sol 3 weight section as a binder, and the ion-exchange-water 40 weight section, preparing a slurry and being filled up in a cel from the emission close side edge side of DPF, it drew in from the emission appearance side edge side, and was made to adhere to a cell wall. After that It dries at 120 degrees C for 2 hours. It calcinated at 500 degrees C for 2 hours, and the bottom coat layer was formed. A bottom coat layer is per [of DPF] l. It is 120g.

[0030] Then, the nitric-acid solution of the dinitrodiammine platinum of predetermined concentration is prepared, after DPF with a bottom coat layer is immersed, it pulls up, and an excessive drop is dried at blowing off and 120 degree C for 2 hours. It calcinated at 500 degrees C for 1 hour, and Pt was supported in the bottom coat layer. To a bottom coat layer, the amount of support of Pt is 1 % of the weight, and is per [of DPF] l. It is 1.2g.
[0031] it is made to sink into DPF which furthermore has the bottom coat layer which supported Pt for the potassium acetate of predetermined concentration, and the specified quantity of the mixed water solution of an acetic-acid lithium -- 120 degree C -- after 2-hour desiccation It calcinated at 500 degrees C for 1 hour, and K and Li were supported. This formed the lower layer 2. DPF is K per l. 0.2 mols and Li 0.1 mols were supported.
[0032] On the other hand, after a mean diameter prepares CeO2 powder which is about 1 micrometer and sinks in the specified quantity of the nitric-acid solution of the dinitrodiammine platinum of predetermined concentration, evaporation to dryness is carried out. Pt/CeO2 powder which calcinated at 500 degrees C for 1 hour, and supported Pt was prepared. The amount of support of Pt is 5 % of the weight.
[0033] The ceria sol and ion exchange water as this Pt/CeO2 powder and a binder are mixed, and a slurry is prepared, and after being filled up in a cel from the inflow side edge side of DPF in which the lower layer 2 was formed, it drew in from the outflow side edge side, and was made to adhere to the front face of a lower layer 2. After that It dries at 120 degrees C for 2 hours. It calcinated at 500 degrees C for 2 hours, and the upper layer 3 was formed. About 30g per l. of DPF is formed, and, for Pt, DPF is [the upper layer 3] abbreviation per l. 1.5g is supported. That is, the amount of support of Pt per l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 2.7g.
[0034] (Example 2) A lower layer 2 and the upper layer 3 were formed like the example 1 except having made the amount of support of Pt of a lower layer 2 into 2 % of the weight to the lower layer 2. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 3.9g.
[0035] (Example 3) A lower layer 2 is received in the amount of support of Pt of a lower layer 2. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 2.9 % of the weight. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 5.0g.
[0036] (Example 4) It is abbreviation to the upper layer 3 about having made the amount of support of Pt of a lower layer 2 into 2 % of the weight to the lower layer 2, and the amount of support of Pt of the upper layer 3. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 8.7 % of the weight. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 5.0g.
[0037] (Example 5) A lower layer 2 is received in the amount of support of Pt of a lower layer 2. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 3.9 % of the weight, and having made the amount of support of Pt of the upper layer 3 into about 1 % of the weight to the upper layer 3. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 5.0g.
[0038] (Example 1 of a comparison) A lower layer 1 is formed like an example 1, and it replaces with CeO2 powder. The upper layer 2 was formed like the example 1 except having used 2Oaluminum3 powder. The amount of support of Pt per 1l. of DPF is the same abbreviation as an example 1 by the sum total of a lower layer and the upper layer. It is 2.7g.
[0039] (Example 2 of a comparison) It is the amount of formation of a bottom coat layer per 1l. of DPF. Having been referred to as 150g, and the amount of support of Pt in a bottom coat layer Except having considered as 3.3 % of the weight, the lower layer 2 was formed like the example 1, and this was made into the particulate filter of the example 2 of a comparison. The amount of support of Pt per 1l. of DPF It is 5.0g.

[0040] <A trial and evaluation> It is displacement about each above-mentioned filter. It attaches in the exhaust air system of the diesel power plant of 4.2L, respectively, and is entering gas temperature. The durability test of 50 hours was performed at 650 degrees C. Next, each filter after a durability test is attached in the exhaust air system of the diesel power plant of displacement 2L, respectively, and it is entering gas temperature. It operated at 350 degrees C for 3 hours. They are a discharge per unit time amount of a diesel particulate at this time (W0), and 2.9 g/an hour.
[0041] Each filter after the above-mentioned trial It dried at 120 degrees C for 4 hours, and the weight (W1) was measured, respectively. In subsequently, the inside of an electric furnace The diesel particulate which

heated for 2 hours and has been deposited at 500 degrees C was burned, and subsequent weight (W2) was measured, respectively. From these values, by the degree type, the combustion rate of a diesel particulate is computed, respectively and a result is shown in Table 1.

[0042]

each filter after measuring combustion rate (%) =(W1-W2) (/(3xW0)) x 100, next a combustion rate is again attached in the exhaust air system of the diesel power plant of displacement 2L, respectively -- the exhaust gas burned on condition that [rich] A/F=12 -- entering -- gas temperature 600 degrees C -- for 15 minutes -- passing -- NOx NOx by which occlusion was carried out to occlusion material Reduction desorption was carried out. After that It changes to Lean operation of A/F=35 and is entering gas temperature. NOx in 300 degrees C The amount of occlusion was measured. A result is shown in Table 1.

[0043]

[Table 1]

	下層				上層			全体の		
	酸化物	コート量 (g/L)	NO_x 吸蔵材	Pt担持量 (重量%)	酸化物	コート量 (g/L)	Pt担持量 (重量%)	Pt担持量 (g/L)	燃焼率 (%)	NO_x 吸蔵量 (mg/L)
実施例1				1.0	CeO_2		5.0	2.7	72	290
実施例2	Al_2O_3		K:0.2	2.0	CeO_2		5.0	3.9	81	320
実施例3	+	120	モル/L	2.9	CeO_2	30	5.0	5.0	86	390
実施例4	TiO_2		Li:0.1	2.0	CeO_2		8.7	5.0	93	340
実施例5	+		モル/L	3.9	CeO_2		1.0	5.0	60	310
比較例1	ZrO_2			1.0	Al_2O_3		5.0	2.7	66	180
比較例2		150		3.3	—	—	—	5.0	58	260

[0044] compared with the example 3 of a comparison which is the conventional configuration, the inflammable ability of a diesel particulate is boiling the filter of examples 1-4 markedly, and is improving. This is considered that it has contributed greatly that the active spot of Pt in the upper layer 3 exists mostly also in after elevated-temperature durability and that the oxygen from CeO2 was supplied with the filter of each example. The effectiveness of CeO2 is clear also from the result of an example 1 and the example 1 of a comparison.

[0045] NOx It is NOx after durability, so that there are many amounts of support of lower layer Pt fundamentally, since occlusion reduction is performed in a lower layer. The amount of occlusion increases. However, it compares with the example 2 of a comparison, and the filter of examples 1-5 is NOx after durability. There are many amounts of occlusion and the correlation with the amount of support of Pt is not seen here. That is, for the filter of an example, the amount of support of Pt is NOx at least than the example 2 of a comparison. There are many amounts of occlusion and CeO2 of the upper layer 3 is NOx. Having controlled sulfur poisoning of occlusion material is guessed.

[0046] If the amount of support of Pt of the upper layer 3 is made fewer than a lower layer 2 still like an example 5, it is also distinct that the inflammable ability of a diesel particulate is falling.

[0047]

[Effect of the Invention] That is, it is NOx while the fall of the inflammable ability of a diesel particulate accompanying reduction of the amount of support of noble metals is controlled according to the particulate filter of this invention. Sulfur poisoning of occlusion material is also controlled.

[Translation done.]

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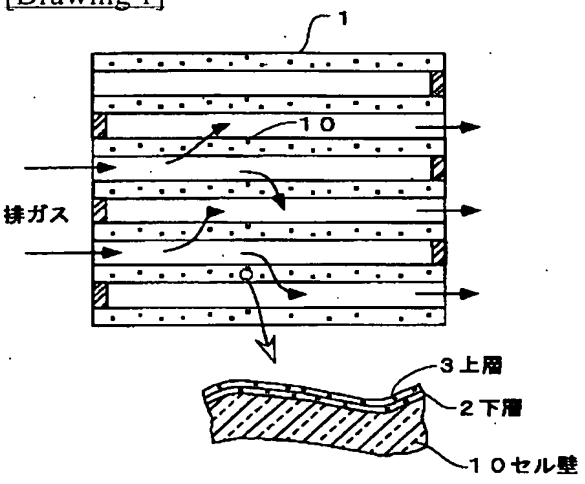
DRAWINGS

[Drawing 1]



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